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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF NANO-STRUCTURE CDO:Y THIN FILMS BY SOL-GEL SPIN COATING METHOD

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ABSTRACT

Thin films of yttrium (Y) doped cadmium oxide (CdO) were prepared on glass substrate by sol-gel spin coating method. The effects of yttrium concentration on structural, optical, morphological and electrical properties of CdO thin films were examined. XRD revealed the prepared films to have a polycrystalline with cubic structure. The scanning electron microscopes of the films show uniform distribution of spherical aggregates composed of nano particles. EDX spectra confirm the presence of cadmium and yttrium elements in prepared film. All the films present a low transmittance in the visible region and the optical band gap decreased from 2.23 to 2.06 eV with increasing yttrium concentration. A Photoluminescence measurement shows UV and blue green emission spectrum. The minimum electrical resistivity and maximum carrier concentration were obtained for 7.5 and 10 wt% of yttrium doped cadmium oxide films respectively.

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INTRODUCTION

Thin films of Transparent Conductive Oxides (TCO) such as tin oxide, zinc oxide and cadmium oxides have been extensively studied because of their applications in semiconductor optoelectronic devices. Among these materials, the Cadmium Oxide (CdO) has been considered a promising material due to high electrical conductivity and used for various applications including gas sensor (Salunke et al., 2009), solar cells (Seval aksoy et

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al., 2009), and optoelectronic devices (Carbelleda-Galicia et al., 2000). Un-doped and doped CdO films have been prepared by different methods such as Chemical bath deposition (De leon-Gutierrez et al., 2006), Magnetron sputtering (Qiang Zhou et al., 2007), Pulsed laser deposition (Gupta et al., 2008), and Spray pyrolysis method (Azizar Rahman & Khan, 2014). The above mentioned techniques are expensive and require high vacuum and stringent conditions. As compared to these methods, the sol-gel process is simple, inexpensive and non-vacuum for synthesizing films (Seval aksoy et al., 2009; Carbelleda-Galicia et al., 2000). The electrical and optical properties of CdO film can be controlled by doping of metallic ion with smaller ionic radius such as Sn (Zheng et al., 2011) and Ga (Deokate et al., 2010). The ionic radius of Y^{3+} (0.90Å) with 6 coordination number is slightly smaller than Cd^{2+} (0.95Å), thus we expect that doping of yttrium with CdO will lead to improvement in electrical conductivity of CdO by increasing electron concentrations (Shannan, 1976). In the present paper, we are reporting the effect of doping concentrations on structural, morphological, optical, photoluminescence and electrical properties of yttrium doped cadmium oxide (CdO:Y) thin films by sol-gel spin coating method.

EXPERIMENTAL

Cadmium acetate di-hydrate [$Cd(CH_3COO)_2.2H_2O$], Yttrium tri-chloride [YCl_3], 2-methoxyethanol and mono-ethanolamine were used as starting material, solvent and stabilizer respectively. First the cadmium acetate di-hydrate was dissolved in 2-methoxyethanol and then mono-ethanolamine was slowly added under magnetic stirrer to prepare a solution of 0.2 M. The molar ratio of mono-ethanolamine to Cadmium acetate di-hydrate was maintained at 1.0. The yttrium dopant was added to solution in the form of yttrium tri-chloride so that the [Y]/[Cd] ratio varied from 0 to 10wt%. The solution was stirred at 60°C temperature for around 1h to yield clear homogeneous solution. The solution dropped on cleaned glass substrate which rotated at 2000 rpm for 30 s using a spin coater. After the coating, the film was dried at 150°C for 10 min to evaporate the solvent and remove organic residuals. This procedure was repeated for five times to obtain sufficient thickness and then the films were annealed at 450°C for 1 h in a furnace.

The crystal structure of the prepared films was investigated using X-ray diffractometer (X'pert PROPANalytical) using CuK_α line (1.54060 Å). The surface morphology was obtained from scanning electron microscope (ESEMQUANTA200, FEI-Netherland) and EDX (attached to SEM) was used to estimate the elemental composition. The optical transmittance measurements made using UV- visible spectrometer (Oceans optics HR2000-USA) and thickness was measured by profilometer (SJ-301Mitutoyo). The photoluminescence (PL) measurements were performed using a spectrofluorometer (Cary Eclipse EL08083851) with xenon arc source. The electrical properties were determined from the room temperature Hall measurements in van der pauw configuration (RH2035 PhysTech GmbH).

RESULTS AND DISCUSSIONS

3.1 Structural Analysis

Fig.1 shows the XRD patterns of pure and yttrium doped cadmium oxide thin films prepared by sol-gel spin coating method. All the films show a preferential orientation along

(111) direction without any impurities and secondary phases. The observed diffraction patterns indicate the polycrystalline nature of the CdO with cubic structure on the basis of JCPDS file: 75-0592. With increasing yttrium concentration, the relative intensity of (111) peak increases gradually, suggesting that the crystalline quality of films becomes better, which is also reflected in surface morphology and electrical properties.

Fig. 1: *XRD Patterns of the CdO:Y Films as Function of the Y Concentrations*

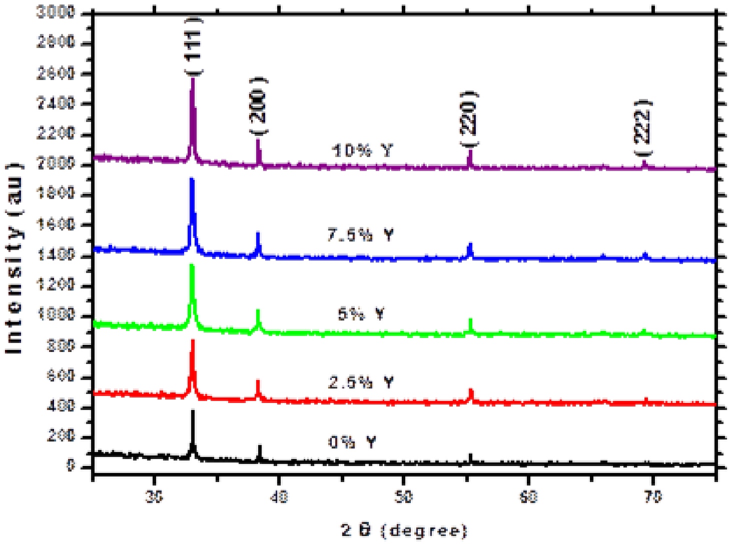
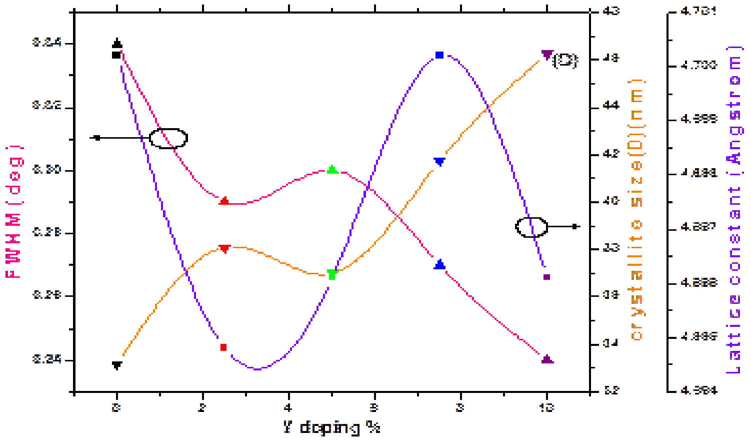


Fig. 2: *The Variation of FWHM, Crystallite Size, Lattice Constants as Function of Y Concentrations*



The crystallite size (D) is calculated using Debye Scherrer's formula (Deokate et al., 2010).

$$D = (0.9\,\lambda) / (\beta \cos\theta)$$

Where D is the crystallite size, **β** is the full width at half maximum (FWHM) **λ** is the X-ray wavelength (1.54060 Å) and **θ** is the Bragg's diffraction angle. The obtained crystallite size decreases with increasing Y concentration. The variation of FWHM, crystallite size and lattice constants are plotted as function of Y doping concentration are shown in Fig.2. The calculated crystallite size, d-spacing and lattice constants were well fitted with JCPDS (75-0592) file data as shown in Table.1. The slight change of lattice constant is due to the change in inter atomic spacing which results arises from substitution of smaller Y^{3+} ions into larger Cd^{2+} ions (Ahmad et al., 2014).

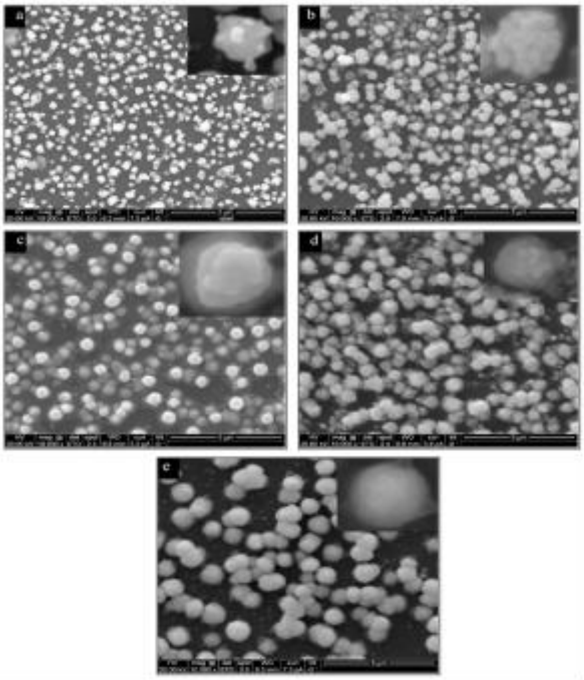
Table 1: *Structural Parameters of Yttrium Doped CdO Thin Films*

Sample	2θ (deg)	d-Space (Å)	FWHM (deg)	Average Grain size D (nm)	Lattice constant a (Å)
CdO: Y 0%	32.98	2.7137	0.34	33.14	4.7002
CdO: Y 2.5%	33.02	2.7105	0.29	38.09	4.6941
CdO: Y 5%	33.01	2.7113	0.30	37.00	4.6961
CdO: Y 7.5%	32.98	2.7137	0.27	41.73	4.7002
CdO: Y 10%	33.01	2.7113	0.24	46.25	4.6961
JCPDS (75-0592)	33.02	2.7105	---	---	4.6940

3.2 Surface and Compositional Analysis

Fig.3 shows the SEM images of pure and yttrium doped CdO thin films. It can be seen that all the films have uniform surface morphologies with spherical aggregates composed of nano particles. With increasing yttrium concentration the surface morphology of CdO films changed considerably. When yttrium concentration increase the crystallite size increases gradually, which result is agrees with the XRD analysis mentioned above. Fig.4 shows the EDX (Energy Dispersive X-ray Spectroscopy) spectra of un-doped and yttrium (5 wt %) doped cadmium oxide thin films. It confirms the presence of yttrium and cadmium oxides in prepared thin films. As expected the nominal yttrium concentration in solution is obtained in prepared films, which is ensured from table inserted in the Fig.4.

Fig. 3: *SEM Images of the CdO:Y Films Deposited with Various Y Concentrations: (a) 0wt%, (b) 2.5wt%, (c) 5wt%, (d) 7.5wt% and (e) 10wt%.*



3.3 Optical Properties

Fig.5 shows the room temperature transmittance spectrum of CdO thin films. It can be seen that the average transmittance of all the films is very low. The transmittances get decreased and the optical absorption edges are shifted to higher wavelength with increasing yttrium concentrations. Similar transmittance reduction has been reported already for Sn, Al and Mn doped CdO thin films (Celia et al., 2009; Kumaravel et al., 2010; Dakhel, 2010).

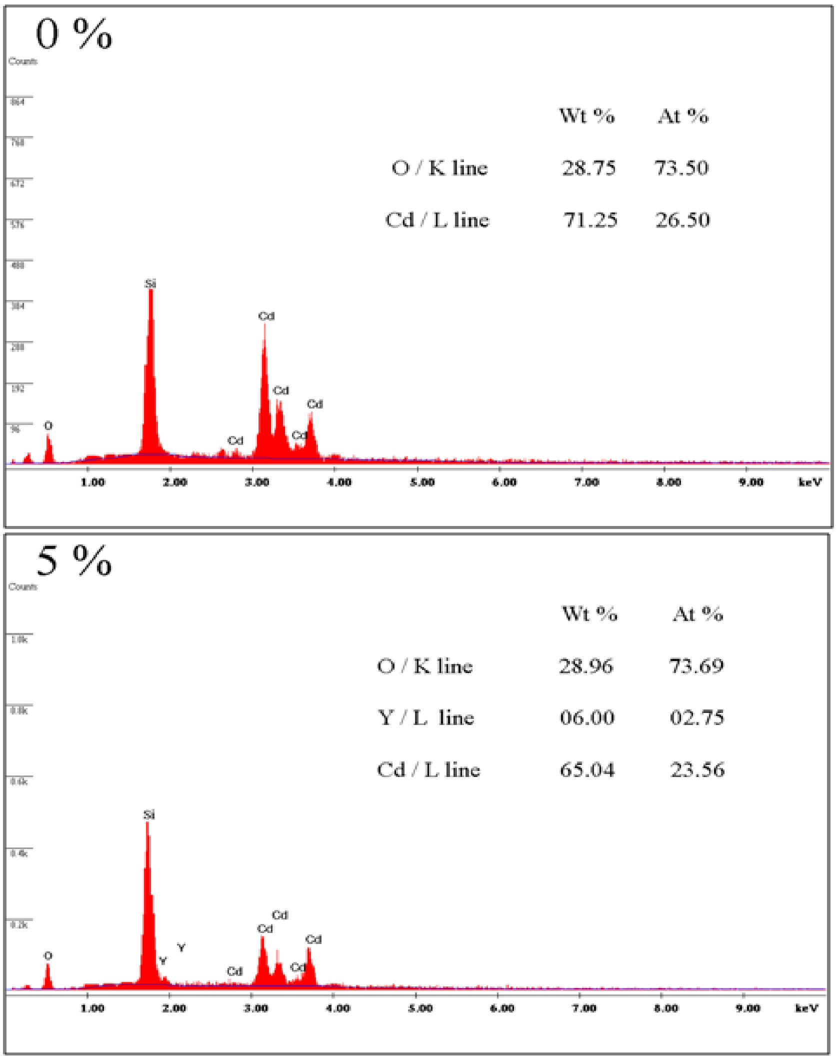
The decrease in the transmittance of film may be due to thickness of the films and absorption of increased free carriers (Wu et al., 1997).

The optical band gap of CdO:Y thin films was estimated by extrapolation of the linear portion of the $(\alpha h\nu)^2$ versus hν plots as shown in Fig.6 using the following relation (Azizar Rahman & Khan, 2014),

$$(\alpha h\nu)^2 = A\,(h\nu - E_g)$$

Where α is the absorption coefficient, hν is the photon energy, A is the constant and E_g is the optical band gap. The obtained band gap values were plotted as a function of yttrium concentration which is shown in Fig.6 (inset). It can be seen that the optical band gap values

Fig. 4: *EDX Spectrum of Un-Doped and 5 wt% of Y Doped CdO Thin Films*



0 %

	Wt %	At %
O / K line	28.75	73.50
Cd / L line	71.25	26.50

5 %

	Wt %	At %
O / K line	28.96	73.69
Y / L line	06.00	02.75
Cd / L line	65.04	23.56

Fig. 5: *Optical Transmittance Spectra of Pure and Y Doped CdO Thin Films*

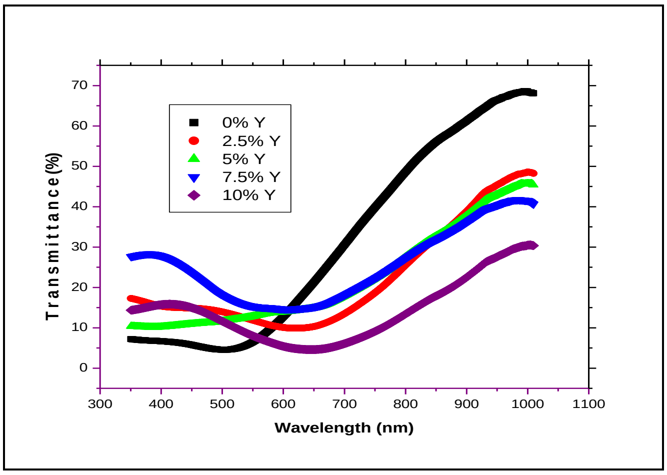
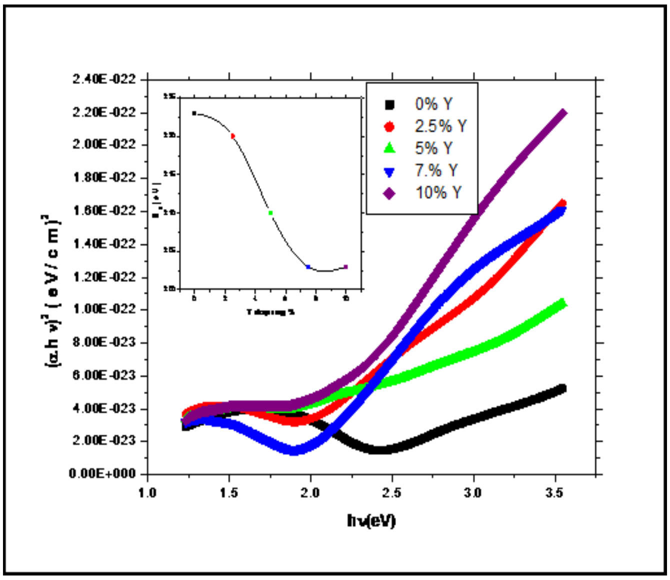


Fig. 6: *The (ahν)² Versus hν Plots and (Inset) Optical Band Gap Values as Function of the Y Concentrations*

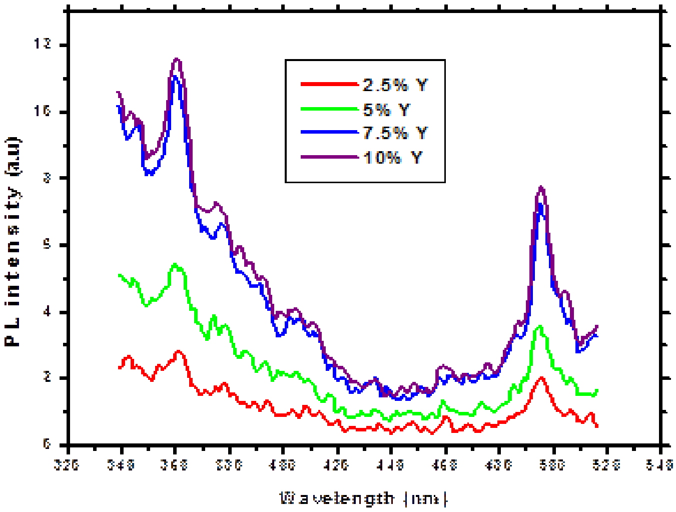


are decreased from 2.23 to 2.06eV with increasing yttrium concentration. Many researchers reported such a decrease in the band gap values after doping (Dakhel, 2010; Maity & Chattopadhyay, 2006) and this value is well matched with the result of Mn doped CdO film (Sankarasubramanian et al., 2014). The narrowing band gap is associated with an increase in the carrier concentration and related to Burstein-Moss effect (Burstein, 1954).

3.4 Photoluminescence Spectra

Fig.7 shows the room temperature photoluminescence spectra of CdO:Y thin films recorded at the excitation wavelength of 317nm. The entire spectrum exhibits mainly two peaks at 360nm and 494nm. Strong UV emission centered at 363 nm are observed for all the samples and can be assigned as a near-band-edge (NBE) emission originating from the recombination of excited electrons from a localized levels below the conduction band with the holes in valence band. A sharp intense peak centered at 494nm corresponding to blue green emission which is arises due to the concentration of free electrons, and the existence of various point defects identified as oxygen vacancy which helps to form the recombination centers (Ghosh & Rao, 2004). The intensity of blue green emission was increases linearly as increasing yttrium concentrations, which may due to the increase of thickness and grain size.

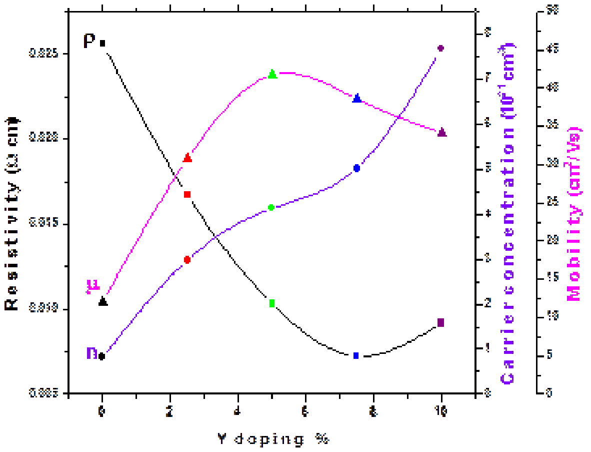
Fig. 7: *Photoluminescence Spectrum of Y Doped CdO Thin Films*



3.5 Electrical Properties

The variation of electrical resistivity (ρ), carrier concentration (n), and mobility (μ) as a function of yttrium doping concentration is shown in Fig.8. The pure cadmium oxide thin film possesses a resistivity 2.56×10^{-2}Ωcm, which decreases rapidly with increasing yttrium doping concentration up to 7.5wt% and then increases slightly for 10wt%. Thus the doping substantially reduces the resistivity to 7.24×10^{-3}Ω-cm for 7.5wt% of yttrium and the carrier concentrations increases from 0.81×10^{21} to 7.68×10^{21}cm^{-3}. The Hall mobility reached a maximum value around 43.7cm^{2}V^{-1}s^{-1} for 5wt% and then slightly decreases with respect to increasing yttrium doping concentration. As compared with electrical parameters of other trivalent cationic materials doped CdO films are presented in Table.1 (Kumaravel et al., 2010; Dakhel, 2010; Maity & Chattopadhyay, 2006; Sankarasubramanian et al., 2014; Dakhel, 2008; Shufang Wang et al., 2013), the obtained carrier concentrations are higher.

Fig. 8: *Resistivity (ρ), Carrier Concentration (n) and Mobility (μ) of the Films as a Function of the Y Concentration*



The electrical resistivity is similar to the reported value (Dakhel, 2010; Sankarasubramanian et al., 2014) and lowers than Ga doped CdO thin film by thermal evaporation method (Dakhel, 2008). The obtained Hall mobility of prepared films is higher than the Fe (Dakhel, 2010), Mn (Sankarasubramanian et al., 2014) and Ga (Dakhel, 2008) doped CdO thin films. These results indicate that the electrical parameters of prepared CdO films are sensitive to yttrium addition. The increase of carrier concentration by yttrium doping can explain as follows: i) the yttrium have one valence electron more than the cadmium atom and ii) the yttrium substitutes the cadmium atom or it occupies the interstitial sites in the CdO lattice (Saha et al., 2007).

Table 2: *Comparison of Electrical Properties of Other Cationic Metals Doped CdO Films*

Films	Preparation method	Carrier concentrations (cm^{-3})	Mobility (cm^3/Vs)	Resistivity (Ω cm)	Reference
CdO	Sol-gel	0.81×10^{21}	12.12	2.56×10^{-2}	Present work
CdO:Y(7.5wt%)	Spin coating	5.05×10^{21}	38.64	7.24×10^{-3}	
CdO	Thermal evaporation	5.28×10^{19}	8.85	1.33×10^{-2}	[20]
CdO:Ga(3at%)		3.15×10^{19}	8.63	2.30×10^{-2}	
CdO	Spray pyrolysis	8.67×10^{19}	68	1.05×10^{-3}	[13]
CdO:Al(3wt%)		4.12×10^{20}	55	3.40×10^{-4}	
CdO:Al(3.5wt%)	Sol-gel Dip coating	0.85×10^{20}	190	2.66×10^{-3}	[16]
CdO	Solid state reaction	1.50×10^{19}	133	5.80×10^{-3}	[21]
CdO:Er(1.5at%)		1.76×10^{20}	232		
CdO	Vacuum evaporation	4.42×10^{19}	7.1	20×10^{-3}	[14]
CdO:Fe(3wt%)		12.2×10^{19}	23.8	2.2×10^{-3}	
CdO	Spray pyrolysis	1.87×10^{20}	8.9	3.73×10^{-3}	[17]
CdO:Mn(3wt%)		14.0×10^{20}	16.2	2.01×10^{-3}	

CONCLUSION

Un-doped and yttrium doped CdO thin films were successfully prepared by sol-gel spin coating method. The XRD spectrum confirmed that the films are polycrystalline with a cubic structure. The SEM micrograph shows uniform distribution of spherical aggregates composed of nano particles. EDX spectrum was confirming the incorporation of yttrium content in the prepared CdO thin films. The UV-vis analysis showed that the yttrium concentration in the films affect the optical band gap and transmittance. PL intensity of blue green emission around 494nm indicates the presence of various point defects. The lowest resistivity, highest carrier concentration and higher mobility were obtained for 7.5, 10 and 5wt% yttrium doped films respectively. From the results, it is clear that the yttrium is sufficiently effective to control the structural, electrical and optical properties of CdO thin films like other metallic dopants.

REFERENCES

[1] Ahmad,T., Khatoon,S., Lofland,S.E., Thakur,G., (2014). Structural characterization and properties of nano-sized $Cd_{1-X}Co_X$ dilute magnetic semiconductors prepared by solvothermal method. *Materials Science and Semiconductor Processing* 17, 207-215.

[2] Azizar Rahman,M., Khan,M.K.R., (2014). Effect of annealing temperature on structural, electrical and optical properties of spray pyrolytic nanocrystalline CdO thin films. *Materials Science and Semiconductor Processing* 24, 26-33.

[3] Burstein,E., (1954). Anomalous optical absorption limit in InSb. *Physics Review* 93, 632.

[4] Carbelleda-Galicia, D. M., Castanedo-Perez, R., Jimenez-Sandoval, O., Jimenez-Sandoval, S., Torres-Delgado, G., Zuniga-Romero, C. I., (2000). High transmittance CdO thin films obtained by sol-gel method. *Thin Solid Films*. 371, 105-108.

[5] Celia M.Ronconi., Oswaldo L.Alves., Roy E.Bruns., (2009). Factorial design preparation of transparent conducting oxide thin films. *Thin Solid Films*. 517, 2886-2891.

[6] Dakhel,A.A., (2010). Electrical and optical properties of Iron doped CdO thin films. *Thin solid films* 518, 1712-1715.

[7]Dakhel,A.A., (2008). Correlated transport and optical phenomena in Ga-doped CdO films. *Solar Energy* 82, 513-519.

[8] De leon-Gutierrez, L.R., Cayente-Romero, J.J., MPeza-Tapia, J., Barrera-Calva, E., Martinez-Flores, J.C., Ortega-Lopez, M., (2006). Some physical properties of Sn-doped CdO thin films prepared by chemical bath deposition. *Materials Letter* 60, 3866-3870.

[9] Deokate,R.J., Salunkhe,S.V., Agawane,G.L., Pawar,B.S., Pawar,S.M., Rajpure,K.Y., Moholkar,A.V., Kim,J.M., (2010). Structural, optical and electrical properties of chemically sprayed nanosized gallium doped CdO thin films. *Journal of Alloys and Compound* 496, 357-363.

[10] Ghosh,M., Rao,C.N.R., (2004). Solvothermal synthesis of CdO and CuO nanocrystals. *Chemistry and Physics Letter* 393, 493-497.

[11] Gupta,R.K., Ghose,K., Patel,R., Mishra,S.R., Kahol,P.K., (2008). Structural optical and electrical properties of In doped CdO thin films for optoelectronic applications. *Materials Letter* 62, 3373-3375.

[12] Kumaravel,R., Menaga,S., Regina Mary Snega,S., Ramamoorthi,K., Jeganathan,K., (2010). electrical, optical and structural properties of aluminum doped cadmium oxide thin films prepared by spray pyrolysis technique. *Material Chemistry and Physics* 122, 444-448.

[13] Maity,R., Chattopadhyay,K.K., (2006). Synthesis and characterization of aluminum doped CdO thin films by sol-gel process. *Solar Energy Materials and Solar Cells* 90, 597-606.

[14] Qiang Zhou., Zhenguo Ji., BinBin Hu., Chen Chen., Lina Zhao., Chao Wang., (2007). Low resistivity transparent conducting CdO thin films deposited by DC reactive magnetron sputtering at room temperature. *Materials Letter* 61, 531-534.

[15] Saha,B., Das,S., Chattopadhyay,K.K., (2007). Electrical and optical properties of Al doped cadmium oxide thin films deposited by radio frequency magnetron sputtering. *Solar Energy Materials and Solar Cells* 91, 1692-1697.

[16] Salunke,R.R., Dhawale,D.S., Dubal,D.P., Lokhande,C.D., (2009). Sprayed CdO thin films for liquefied petroleum gas (LPG) detection. *Sensors and Actuators B* 140, 86-91.

[17] Sankarasubramanian,K., Soundararajan,P., Logu,T., Kiruthiga,S., Sethuraman,K., Ramesh babu,R., Ramamurthi,K., (2014). Influence of Mn doping on structural, optical and electrical properties of CdO thin films prepared by low cost effective spray pyrolysis method. *Materials Science Semiconductor Processing* 26, 346-353.

[18] Seval Aksoy., Yasemin Caglar., Saliha Illican., Mujdat Caglar., (2009). Effect of heat treatment on physical properties of CdO thin films deposited by sol-gel method. *International Journal of Hydrogen Energy*. 34, 5191-5195.

[19] Shannan,R.D., (1976). Revised effective ionic radii and systematic studies of inter atomic distances in halides and chalcogenides. *Acta Crystallography* A32, 751-767.

[20] Shufang Wang., Fuqiang Liu., Qing Lu., Shouyu Dai., Jianglong Wang., Wei Yu., Guangsheng Fu., (2013). The effect of Er^{3+} doping on the structural and thermoelectric properties of CdO ceramics. *Journal of European Ceramic Society* 33, 1763-1768.

[21] Wu,X., Coutts.T.J., Mulligan,W.P., (1997). Properties of transparent conducting oxides formed from CdO and ZnO alloyed with SnO_2 and In_2O_3. *Journal of Vacuum Science and Technology* A15, 1057-1062.

[22] Zheng,B.J., Lian,J.S., Zhao,L., Jiang,Q., (2011). Optical and electrical properties of Sn-doped CdO thin films obtained by pulsed laser deposition. *Vacuum* 85, 861-865.